Speciation of Technetium in Borosilicate Glasses Prepared in Air

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ABSTRACT

A series of glass samples were prepared analogous to high level waste glass using either glass frit or glass precursors combined with a high level waste surrogate containing $NaTcO_4$. Three different technetium species were observed in these glasses depending upon the synthesis conditions. If the glasses were prepared by reducing $NaTcO_4$ to $TcO_2 \cdot 2H_2O$ with hydrazine or if a large amount of organic material was present, inclusions of TcO_2 were observed. If no organic material was present, technetium was incorporated as TcO_4^-. If only a small amount of organic material was present, isolated Tc(IV) sites were observed in the glass. The relative technetium retention of these glasses was estimated from the Tc K-edge height, and had no correlation with the oxidation state of the technetium. Pertechnetate was well retained in these glasses.

INTRODUCTION

Borosilicate glass is the major waste form for the immobilization of the legacy high level nuclear waste created by years of plutonium production by the DOE. Glass was selected for several reasons including good durability and the fact that vitrification is a mature technology. Although most radionuclides present no challenges to the vitrification of high-level waste, certain radionuclides, especially ^{137}Cs and ^{99}Tc, are easily volatilized during vitrification.[1]

The behavior of technetium and rhenium in borosilicate glasses has been reviewed,[2] and will be discussed only briefly. A number of Tc(VII) compounds have low boiling points. Both pertechnetyl chloride and fluoride (TcO_3Cl and TcO_3F) have boiling points under 100 °C. Tc(VII) oxide, Tc_2O_7, boils at 350 °C, and the alkali metal salts of pertechnetate, particularly $CsTcO_4$, are volatile at high temperature. Little is known about the speciation of technetium in these glasses. Two studies about the speciation of technetium in borosilicate glasses have been reported.[1,3] Under reducing conditions, the glasses contained technetium metal, and under oxidizing conditions, the glasses contained TcO_2 inclusions. In none of these experiments was Tc(VII) observed. While these results may seem to imply that Tc(VII) is not stable in glass (presumably due to loss of volatile Tc(VII) species), the conditions used to prepare the glasses are not representative of those used to prepare actual waste form glasses, so the technetium speciation in these glasses may by different from those prepared under conditions more similar to those used for actual waste.

The main focus of this research is to characterize the speciation of technetium in borosilicate glasses as a function of experimental conditions, especially conditions

similar to those used to prepare actual waste glasses: vitrification of mixture of glass precursors and simulated waste.

EXPERIMENTAL DETAILS

Caution: ^{99}Tc is a β-emitter (E_{max} = 294 keV, $\tau_{1/2}$ = 2 × 10^5 years). All operations were carried out in a radiochemical laboratory equipped for handling this isotope. The concentration of sodium pertechnetate was determined spectrophotometrically at 289 nm (e = 2380 M l^{-1} cm^{-1}). UV-visible spectra were obtained using an Ocean-Optics ST2000 spectrometer. X-ray absorption fine structure (XAFS) spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at Beamline 4-1 using a Si(220) double crystal monochromator detuned 50% to reduce the higher order harmonic content of the beam. All ^{99}Tc samples were triply contained inside sealed polyethylene vessels.

All operations were carried out in air. Water was purified using a MilliQ system. All other chemicals were used as received. Several series of glass samples were prepared using similar conditions. A waste simulant containing NaTcO$_4$ was added to either powdered glass frit or glass precursors forming a thick slurry, which was transferred to a small 5%Au/Pt crucible. In some cases, the NaTcO$_4$ was initially reduced to TcO$_2$•2H$_2$O using hydrazine. In addition, certain components of the waste simulant, such as nitrate or EDTA, were omitted in selected experiments. The crucible was suspended in a vertical tube furnace. In a typical experiment, the furnace was heated to 90 °C at 6 °C/min then to 110 °C at 0.75 °C/min then to 1200 °C at 10 °C/min and held at 1200 °C for 30 min. The glass was allowed to cool to room temperature inside the furnace. The final glass compositions, and the compositions of the waste simulants are listed in Table 1.

X-ray absorption fine structure spectra (XAFS) were obtained in the transmission mode at room temperature using Ar filled ionization chambers and in fluorescence yield mode using a multi-pixel Ge-detector system.[4] The spectra were energy calibrated using the first inflection point of the pre-edge peak from the Tc K edge spectrum of an aqueous solution of NH$_4$TcO$_4$ defined as 21044 eV. EXAFS analysis and radiolysis experiments were carried out as previously described.[5]

RESULTS AND DISCUSSION

Two series of glass samples were prepared, and their compositions are given in Table 1. The first series consists simple borosilicate glasses prepared from oxide and carbonate precursors plus a very simple waste simulant consisting of sodium hydroxide and sodium aluminate with and without added EDTA. Technetium was added as either NaTcO$_4$ or TcO$_2$•2H$_2$O. The second series glasses have compositions more representative of low activity waste glass, and the waste simulant is an SY-101 simulant in which technetium is the only radioactive component.[6] The final composition of the glasses and the composition of the waste surrogates are given in Table 1.

Table 1. Composition of glasses and waste simulants

Final Glass Composition (wt %)	Waste Simulant Composition (M)
Simple Borosilicate Glasses	
63 SiO_2, 15 Al_2O_3, 14 Na_2O, 4 B_2O_3, 4 CaO, 0.2 TcO_2	4M NaOH, 1M $NaAlO_2$, 0.28M EDTA[a]
Simulated Hanford Low Activity Waste Glass	
40 SiO_2, 30 Na_2O, 6 B_2O_3, 6 Al_2O_3, 5 Fe_2O_3, 3 ZnO, 2 ZrO_2, 2 TiO_2, 2 CaO, 2 K_2O, 1 MgO, 0.2 Cs_2O, 0.2 TcO_2	5M NaOH, 0.5M $NaAlO_2$, 0.5M KOH, 0.2M KF, 0.05M Na_2SO_4, 0.02 CsCl, 0.02M Na_2HPO_4, 3.2M $NaNO_3$[a], 1.2M $NaNO_2$[a], 0.08M EDTA[a]

a) not present in all simulants

Three different technetium environments were observed in these glass samples. In general, technetium was present as two of these three species in any given glass sample. In a few samples, the great majority of the technetium was present as a single species. In these cases, EXAFS was used to determine the local structure of the technetium coordination environment. The EXAFS spectra of these species are shown in Fig. 1 along with the local structure determined from the EXAFS data. Table 2 contains the structural parameters derived from the EXAFS data.
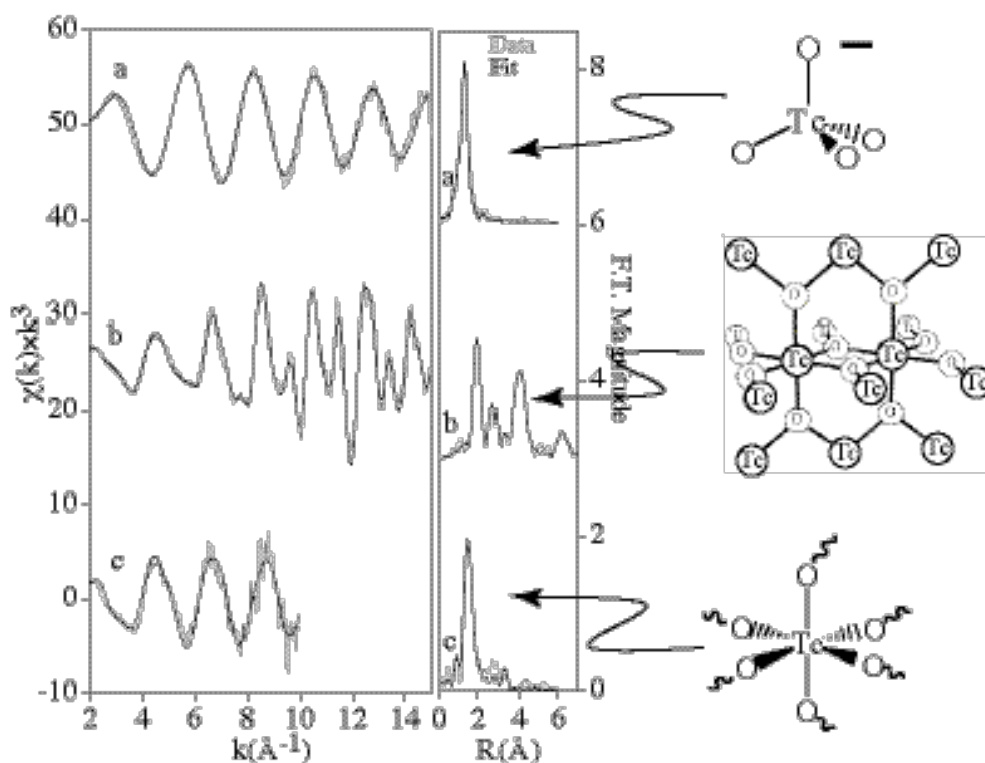
Figure 1. Tc K-edge EXAFS spectra and Fourier Transforms (left) and corresponding local environments (right) of (a) pertechnetate, (b) crystalline TcO_2 inclusions, and (c) isolated Tc(IV) centers (Tc-oct) in a glass matrix. Data are shown in gray and fits are shown in black.

Table 2. EXAFS fitting parameter for technetium species in glass

Scattering Path	Coordination Number	Distance (Å)	Debye-Waller Parameter (Å^2)	DE$_0$ (eV)
TcO$_4^-$ in glass, Scale Factor = 0.92(2)				
Tc-O	4[a]	1.723(1)	0.0024(1)	-6.3(5)
TcO$_2$ inclusions in glass, Scale Factor = 0.73(5)				
Tc-O[c]	1.3(3)	1.70(1)	0.003(1)	-11(4)
Tc-O	6[a]	1.994(3)	0.0019(3)	-6(1)
Tc-O-Tc-O[d]	6[a]	4.06(3)	0.0019[b]	-6[b]
Tc-Tc	1[a]	2.597(3)	0.0033(3)	-6[b]
Tc-Tc	1[a]	3.095(4)	0.0026(4)	-6[b]
Tc-Tc	9[a]	3.645(3)	0.0050(2)	-6[b]
Tc-Tc	3[a]	4.54(1)	0.0064(8)	-6[b]
Tc-Tc	9[a]	5.434(6)	0.0048(4)	-6[b]
Tc(IV) in glass (Tc-oct), Scale Factor = 0.82(6)				
Tc-O	6[a]	2.031(4)	0.0045(7)	0.6(8)
Tc-O-Tc-O[d]	6[a]	4.17(3)	0.001(4)	0.6[b]

a) Coordination number fixed.
b) Parameter linked to previous parameter.
c) Separate Tc-O shell due to TcO$_4^-$ in sample.
d) Four-legged multiple scattering path due to *trans* oxygen ligands.

The technetium environment most often observed among these samples is pertechnetate, shown in Fig. 1a. The Tc-O distance is typical of pertechnetate, and no other scattering paths are observed for this species, which is typical even when pertechnetate is adsorbed on solid matrices. This observation is in agreement with electrochemical investigations technetium oxidation state in borosilicate melts reported by Freude, et al. who show that Tc(VII) is present in glass melts in equilibrium with air.[7] In addition, the environment shown in Fig. 1a is clearly TcO$_4^-$ and not Tc$_2$O$_7$, which would have a distinct Tc-Tc scattering path in its EXAFS spectrum.

The other commonly observed technetium environment found in these examples is Tc(IV) octahedra homogenously distributed in the glass matrix (Tc-oct), illustrated in Fig. 1c. Unfortunately, the signal to noise ratio of the spectrum in Fig. 1c is poor due to intense fluorescence from the 2 wt% ZrO$_2$ in this sample, which limited the technetium fluorescence signal. Consequently, the k-range of this data is severely limited. The only scattering paths observed for this species are due to the TcO$_6$ coordination environment. The 2.03 Å bond distance is typical for at Tc(IV) center with oxygen ligands.[5] Scattering by more distant neighbors is not observed due to the truncation of the data.

The least commonly observed environment is inclusions of crystalline TcO$_2$.[8] The spectrum shown in Fig. 1b illustrates this environment, which is clearly identified by Tc-Tc scattering distances identical to those of crystalline TcO$_2$. [8] In addition, the sample shown in Fig. 1b also contains some pertechnetate. Crystalline TcO$_2$ inclusions were previously observed by Antonini, et al. in glasses prepared using NH$_4$TcO$_4$.[3]

The identities of the technetium species found in the glasses appear to result directly from the preparation conditions. Easiest to explain is the origin of TcO_2 inclusions. These occur when a technetium compound that is a precursor to TcO_2 is used to prepare the glass sample. The most obvious of these precursors is $TcO_2 \cdot 2H_2O$, which is converted to $TcO_2(cr)$ at a relatively low temperature, 300 °C.[9] The less obvious precursor is NH_4TcO_4, which is also converted to $TcO_2(cr)$ by heating to 350 °C under an inert atmosphere.[10] $TcO_2 \cdot 2H_2O$ can be generated either by initially reducing TcO_4^- with hydrazine or by including a large excess of organic material in the waste simulant. Both routes were observed to yield glasses containing $TcO_2(cr)$ inclusions in the experiments reported here. In addition, the work of Antonini, et al. illustrates the formation of $TcO_2(cr)$ inclusions from the decomposition of NH_4TcO_4..[3]

The other two technetium environments observed in these experiments are believed to result from initial incorporation of pertechnetate in the melt. As illustrated in Fig. 1a and observed in many of these samples, pertechnetate added to the glasses is incorporated as pertechnetate provided that it is not reduced, either by organic materials in the waste surrogate or by other routes, such as decomposition of NH_4TcO_4. If the glass precursor contains a small amount of organic material, Tc(IV) homogeneously distributed in the glass matrix, Tc-oct, is observed. This species presumably results from initial incorporation of pertechnetate in the melt, followed by reduction of pertechnetate in the melt. The identity of the reducing agent is currently unknown, but could be either residual carbonaceous material resulting from the pyrolysis of organic components in the waste surrogate or Fe(II) created by reduction by the same organic components. The latter seems more likely given the relative fractions of Fe and Tc present.

CONCLUSION

The conclusions that can be drawn from this work are the identities of the technetium species present in glasses prepared under conditions analogous to actual waste glasses and the origins of these technetium species. Inclusions of TcO_2 occur if technetium is added to the glass as NH_4TcO_4 or $TcO_2 \cdot 2H_2O$ or if strongly reducing conditions occur at the start of the vitrification process, prior to formation of the melt. If pertechnetate is present when the melt is formed, either TcO_4^- or Tc-oct is present in the glass depending on the electrochemical potential of the melt. In addition, these results show that pertechnetate can be well retained in glasses under certain conditions.

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